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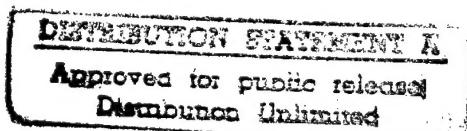
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SOLVENT EXTRACTION SEPARATION
OF URANIUM AND PLUTONIUM
FROM FISSION PRODUCTS

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F. L. Culler and J. R. Flanary

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Oak Ridge National Laboratory, Oak Ridge, Tennessee



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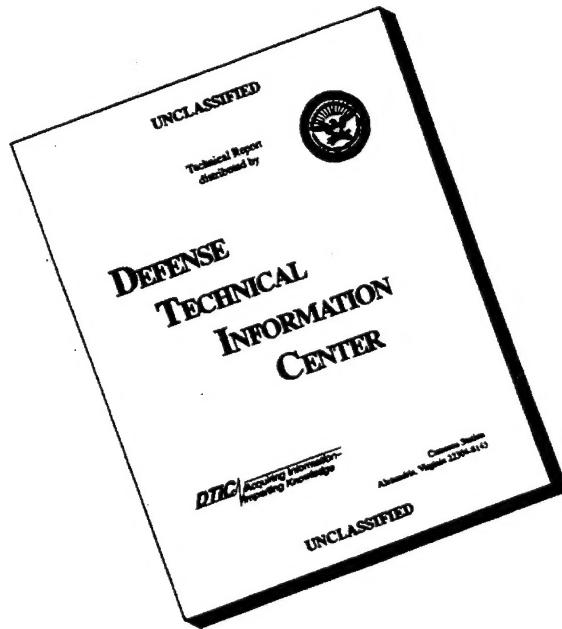
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ABSTRACT

SOLVENT EXTRACTION SEPARATION OF URANIUM
AND PLUTONIUM FROM FISSION PRODUCTS

By

F. L. Culler and J. R. Flanary

American Nuclear Society

Solvent extraction, with tri-*n*-butyl phosphate (TBP) as the solvent and nitric acid as the salting agent, has been utilized as an efficient method for the separation of uranium and plutonium from fission products. A solution of TBP in refined kerosene extracts uranium (VI) and plutonium (IV) from a nitric acid solution of irradiated uranium, leaving the bulk of the fission products in the aqueous phase. The organic phase is then treated successively with fresh nitric acid to remove fission products, with ferrous sulfamate in nitric acid to recover the plutonium which has been reduced to plutonium (III), and finally with water to recover the uranium. At this point the uranium and plutonium have been quantitatively separated from one another. Further decontamination from fission products may be achieved in a second cycle of solvent extraction if required.

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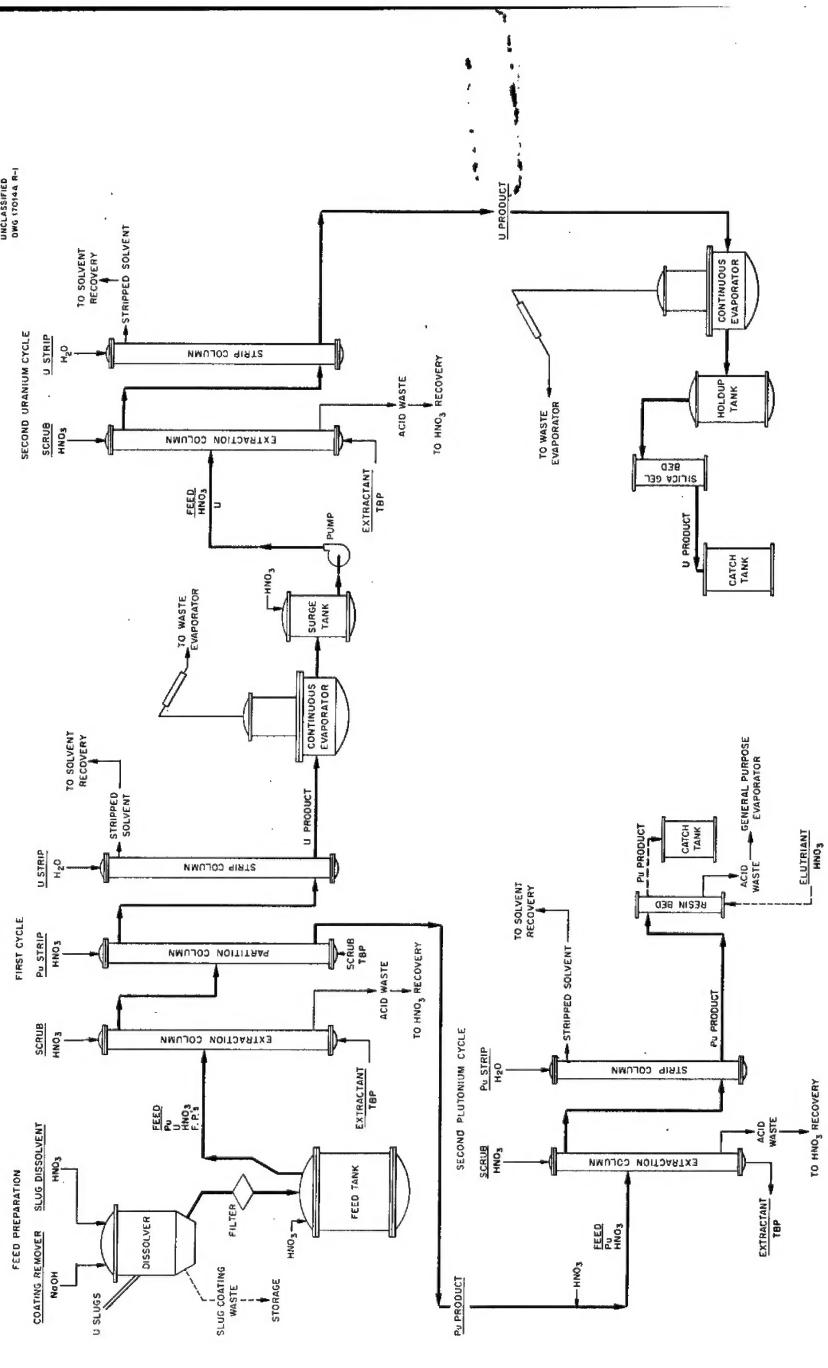
F. L. Culler and J. R. Flanary

A continuous solvent-extraction process has been developed which uses tri-n-butyl phosphate (TBP) as the solvent and nitric acid as the salting agent for the isolation of uranium, plutonium, and fission products from irradiated metallic uranium reactor fuel. Tributyl phosphate is less volatile and has a higher flash point than methylisobutyl ketone used in earlier processes. Nitric acid can be distilled off and reused in the process; this yields a lower waste volume than when aluminum nitrate is used as the salting agent.

The fuel rods, after irradiation, contain a nearly equivalent weight of plutonium and mixed fission products which are a small fraction of the uranium present. Processing this irradiated uranium, after 90 to 120 days' standing to permit decay of short-lived radio-elements, by the flowsheet (Fig. 1) has given the following beta and gamma activity decontamination factors for uranium and plutonium:

After 2 Cycles of Solvent Extraction

	β	γ
U	6.6×10^6	2.7×10^6
Pu	7.7×10^6	2.0×10^6



After 2 Cycles of Solvent Extraction
Plus Adsorption

	β	γ
U	9.9×10^6	6.5×10^6
Pu	3.2×10^7	1.6×10^7

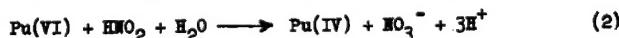
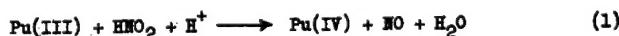
PROCESS STEPS

All steps in the process except feed preparation are continuous, and recent developments indicate that continuous feed preparation may be feasible. Pulse columns are used for contacting the organic and aqueous phases and have proved to be very efficient and reliable. The process consists of the following steps: (1) fuel dissolution and feed adjustment; (2) first cycle extraction, partitioning, and stripping of uranium and plutonium; and (3) separate second cycles of extraction and adsorption for purification of plutonium and uranium. The solvent is reconditioned and reused.

Fuel Dissolution and Feed Adjustment. The irradiated uranium slugs are charged into a vessel where the aluminum sheath is preferentially dissolved in sodium hydroxide--sodium nitrate solution. The uranium is then dissolved in nitric acid at 105°C. About 4.5 moles of nitric acid is consumed per mole of uranium dissolved. The uranyl nitrate--nitric acid solution is filtered to remove solids (e.g., silica, undissolved aluminum), after which final feed adjustment is made by addition of nitric acid.

Some disproportionation of Pu(IV) to Pu(III) and Pu(VI) occurs during the holdup in the batch dissolution procedure where the acidity

is low prior to adjustment. Therefore, after acid adjustment, nitrous acid is added to convert the plutonium to the Pu(IV) form, which is the most stable and also the most highly complexed by TBP



First Cycle Extraction and Partitioning of Uranium and Plutonium.

The uranium and plutonium are extracted from the metal solution by TBP, diluted with an inert hydrocarbon of low viscosity and specific gravity. The two metals are subsequently separated and each is eventually extracted back into an aqueous medium. In the first extraction the aqueous acidic metal solution enters the column near the midpoint and flows downward; the organic phase enters the bottom of the column and flows upward. Flow conditions and salting strength are so regulated that uranium and Pu(IV) are extracted almost quantitatively, leaving most of the fission products and other impurities in the aqueous phase.

After extracting the metal, the organic phase, which is nearly saturated with uranium, is scrubbed in the upper part of the column with nitric acid to backwash any extracted fission products before it passes out the top and on to the midpoint of the second (partitioning) column. A high degree of saturation is maintained to maximize throughput and restrict fission product extraction. The aqueous solution, containing the bulk of the fission products, is drawn off the bottom of the first column.

In the partitioning column the plutonium is reduced to Pu(III) in the presence of dilute nitric acid, which is introduced at the top of the column. Plutonium(III), which has a very low distribution coefficient, 0.02 under these conditions, and part of the uranium are stripped from the organic solvent into this acid stream. The aqueous stream is scrubbed with TBP, introduced at the bottom of the column, to re-extract the uranium. The aqueous plutonium solution flows continuously to the second plutonium cycle; the organic uranium solution is fed to the bottom of a third column where the uranium is stripped with water, and is then fed to the second uranium cycle. At this point the products are decontaminated from gross fission products by a factor of 10^3 - 10^4 .

Extraction column conditions are chosen for maximum uranium and plutonium and minimum fission product extraction as determined by the relative complexing action of TBP. The reaction of uranyl nitrate with TBP is



$$\text{and } K_m = \frac{\text{UO}_2(\text{NO}_3)_2\text{TBP}_2 \text{ org}}{\text{UO}_2^{++} \text{aq} (\text{NO}_3^-)^2 \text{aq} (\text{TBP})^2 \text{ org}}$$

The equilibrium constant, K_m , for this reaction is nearly independent of hydrogen ion concentration. Similar complexes are formed by TBP with nitric acid and with Pu(IV) and Pu(VI). In nitric acid concentrations greater than 1 M, an equation involving second-power TBP dependence and fourth-power nitrate dependence fits most of the data for Pu(IV).

Equation (3) may be rewritten as

$$U(VI) \text{ D.C.} = K_m (\text{NO}_3^-)^2_{\text{aq}} (\text{TBP})^2_{\text{org}} \quad (4)$$

where the uranium organic/aqueous distribution coefficient, D.C. (O/A), is defined as the ratio of the uranium concentration in the solvent to that in the aqueous phase.

The relative complexing power of TBP is illustrated by the results of batch equilibration of TBP with a nitric acid solution of uranium, plutonium, and mixed fission products, with conditions adjusted to yield about 60% uranium saturation of the solvent. The D.C. (O/A) for U(VI), Pu(IV), and Pu(VI) is 8.1, 1.5, and 0.6, respectively; that for the bulk of the fission products is 0.002. Hence, a high degree of separation is possible.

From Equation (4) it may be seen that the complexing action of TBP is affected by the nitrate ion concentration of the aqueous phase and the concentration of TBP.

Extraction of uranium, Pu(IV) and gross beta activity increases with increasing nitrate ion concentration. With the rare earths the distribution is the opposite (see Table I).

The uranium distribution coefficient (O/A) decreases as uranium saturation of the solvent is approached. Also, with a high uranium saturation less plutonium and fission products are extracted (see Table II). The proper saturation point for maximum decontamination consistent with efficient product extraction is determined from the extraction factor, i.e., the ratio of the amount of product

in the solvent phase to that in the aqueous phase multiplied by the ratio of organic to aqueous flow rates:

$$\text{Extraction factor} = \text{D.C.} \times \frac{\text{vol of organic phase}}{\text{vol of aqueous phase}}$$

Plutonium Purification. For additional separation from fission products, the plutonium is processed through a second solvent-extraction cycle in a manner similar to that previously described. The aqueous Pu(III) solution is treated continuously with a threefold excess of sodium nitrite at room temperature.

After adjustment to the appropriate salting strength with nitric acid the Pu(IV) is then again extracted with TBP.

The organic phase, after scrubbing with nitric acid to backwash extracted fission products, passes to a second column where the plutonium is stripped into water. Final product concentration is achieved by ion exchange.

Uranium Purification. The aqueous stream from the first cycle is continuously evaporated and adjusted to proper feed concentration by addition of nitric acid. This feed is made 0.05 M in sodium nitrite to convert the ruthenium to a relatively inextractable form, probably a nitroso complex.

The uranium is extracted with TBP under conditions similar to those of the first cycle. The uranium is stripped from the organic phase with water, and the aqueous effluent is evaporated. At this point the product meets β -activity specifications, but it contains two to three times the permissible amount of γ activity.

The uranium is finally purified by passing the concentrate through a column packed with silica gel, which adsorbs the residual fission products but is otherwise chemically inert to the influent stream. It also acts as a filter; any insoluble matter present in the concentrate collects near the top of the bed, and is subsequently backwashed when the adsorbed activity is eluted with dilute oxalic acid. Integral decontamination factors of 10 to 30 are obtained by silica gel adsorption.

Table I

Distribution of Uranium, Plutonium, and Fission Products as a Function of Nitric Acid Concentration in the Primary Extraction

Aqueous: nitric acid solution of U, Pu, and mixed fission products

Solvent: TRP in Amoco 123-15

Equilibration time: 5 min; Temperature: 25°C

HNO ₃ in Aqueous Phase (M)	Distribution Coefficient, O/A			
	U	Pu(IV)	Gross β	Total Rare Earths
0.5	1.18	0.10	0.0008	0.0004
2	2.84	0.46	0.0008	0.0005
3	3.28	0.59	0.0010	0.0004
4	4.28	1.11	0.0023	0.0004
5	4.16	1.55	0.0034	0.0002
6	3.61	2.62	0.0041	0.0001

Table II

Distribution of Uranium, Plutonium, and Fission Products as a Function of Percentage Uranium Saturation of Solvent

Aqueous: nitric acid solution of U, Pu, and mixed fission products

Solvent: TRP in Amoco 123-15

Equilibration time: 5 min; Temperature: 25°C

Uranium Saturation of Solvent (%)	Distribution Coefficient, O/A			Total Rare Earths
	U	Pu(IV)	Gross β	
28.0	16.7	4.0	0.013	0.0096
37.0	13.7	3.7	0.011	0.0073
45.6	12.1	2.3	0.0065	0.0048
54.9	10.2	1.3	0.005	0.0032
61.7	7.9	1.6	0.0035	0.0021
70.2	6.4	1.3	0.0025	0.0014
72.0	5.4	1.1	0.0018	0.0011
77.2	4.5	1.0	0.0015	0.0007
82.4	3.6	0.79	0.0011	0.0004
86.8	2.3	0.57	0.0007	0.0002

Table III

Properties of Tributyl Phosphate

Chemical formula	$(C_4H_9)_3PO_4$	Specific gravity at	
Molecular weight	266	25°C	0.973
Color	Water white	Freezing point	-80°C
Odor	Mildly sweet	Flash point, Cleve-	
Refractive index at 20°C	1.4245	land open cup	294°C
Viscosity at 25°C	3.41 centipoises	Dielectric constant	
at 85°F	38.6 Saybolt sec	at 30°C	7.97
Boiling point at		Solubility in water	
760 mm Hg	289°C	at 25°C	0.6 vol %
15 mm Hg	173°C	Solubility of water	
1 mm Hg	121°C	in TRP at 25°C	7 vol %

SOLVENT CHEMISTRY

Pure tributyl phosphate is a water-white, somewhat viscous liquid (see Table IV) used industrially as a plasticizer and antifoaming agent. Early experience with this solvent indicated that the fission product β activity in the first cycle product was five times as great with commercial-grade TBP as with butanol-free TBP. Butanol reduces Pu(IV) to Pu(III) with attendant high loss to the waste. Dibutyl acid phosphate (DBP), which is present in commercial-grade TBP, complexes Pu(IV) and causes excessive losses. However, complexing of Pu(III) by the organic-soluble DBP is relatively weak, and it does not result in appreciable losses in stripping Pu(III). Monobutyl acid phosphate, which is aqueous-soluble, is also present in commercial-grade TBP. No major process difficulties associated with this contaminant have been encountered, although it forms precipitates with Pu(IV). The acidic phosphate impurities and traces of uranium and fission products are easily removed from the used solvent by washing with dilute sodium carbonate or hydroxide solution followed by dilute nitric acid washing. All new and used solvent is treated in this manner before use or reuse.

The TBP concentration is limited by its relatively high viscosity and density. Desirable physical properties are attained by blending the solvent with an inert hydrocarbon of low specific gravity and viscosity to permit greater dispersal and more rapid phase disengagement. The diluent used, Amsco 123-15, has a specific gravity of 0.788, a flash point of 143°F , and a Saybolt viscosity at 100°F of 31 sec. The diluent is composed of 83% paraffins, 11% aromatics, and 6%

naphthenes. Although the diluent becomes yellow upon contact with aqueous streams containing nitrous acid, the extent of nitration under process conditions is very slight and not significant.

The selection of Amsco 123-15 in preference to other hydrocarbons with similar physical properties and chemical compositions was based on the following criteria: (1) high flash point, (2) nontoxicity, (3) noncorrosiveness to stainless steel, (4) purity, (5) radiation stability, and (6) low affinity for fission products.

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